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MATHEMATICS

On the Characteristic Elements of Linear Transformations in Banach Spaces

by

M. ALTMAN

Presented by S. MAZUR on December 15, 1953

The present note contains some theorems concerning the general theory of iteration of linear transformations in Banach spaces. As immediate corollaries of these theorems we obtain a generalization of the results of S. Mazur [1]. Notice that the method of S. Mazur is not applicable in this case.

Let U be a linear (i. e. additive and continuous) transformation which maps a Banach space $\mathfrak{X}$ into itself. Denote by $N(U)$ the set of all solutions of the equation $U(x)=x$, by $M(U)$ the set of all elements of the form $y=x-U(x)$, where $x \in \mathfrak{X}$, by U^k the k-th iteration of U and by $\overline{U}$ the adjoint of U. The closure $\overline{M(U)}$ of $M(U)$ is a linear subspace of $\mathfrak{X}$.

Theorem 1. *If*

1) *the sequence* $\{U^n(x)/n\}$ *converges weakly to* 0 *for any* x *of* $\mathfrak{X}$, *and if*

2) *there exists a constant* C *such that* $\left\|\frac{1}{n}\sum_{k=1}^{n} U^k\right\| \leqslant C$ *for* $n=1,2,\ldots,$

then $N(U)\cdot\overline{M(U)}=0$.

Proof. Suppose that there exists an element $x_0 \in \overline{M(U)}$ such that $U(x_0)=x_0$. Let y_0 be an element of $M(U)$ such that $\|y_0-x_0\| < \varepsilon/2C$, where ε is an arbitrary positive number. Condition 1) implies that the sequence $\left\{\frac{1}{n}\sum_{k=1}^{n} U^k(y_0)\right\}$ converges weakly to 0. By a theorem of S. Mazur ([2], p. 81) there exist numbers $\alpha_n (n=1,2,\ldots,m)$ such that $\alpha_n \geqslant 0$, $\sum_{n=1}^{m}\alpha_n = 1$ and

$$\left\|\sum_{n=1}^{m}\alpha_n \frac{1}{n}\sum_{k=1}^{n} U^k(y_0)\right\| < \frac{\varepsilon}{2}.$$

From 2) it follows that

$$\left\|\sum_{n=1}^{m}\alpha_n \frac{1}{n}\sum_{k=1}^{n} U^k(y_0-x_0)\right\| < \frac{\varepsilon}{2}.$$

Thus we obtain $\|x_0\| < \varepsilon$ and consequently $x_0 = 0$. From theorem 1 follows

Theorem 2. *Under the same assumptions as in theorem 1, we have $p \leqslant q$, where p (or q) is the maximal number of linearly independent solutions of the equation $x - U(x) = 0$ (or of its adjoint equation).*

Proof. Denote by N_m the set of all elements of the form

$$x = a_1 x_1 + a_2 x_2 + \ldots + a_m x_m, \quad \text{where} \quad x_1, x_2, \ldots, x_m$$

are linearly independent solutions from $N(U)$ and a_k $(k = 1, 2, \ldots, m)$ arbitrary numbers, further, denote by $\mathfrak{X}_0$ the set of all elements of the form $x = x' + x''$, where $x' \in N_m$, $x'' \in \overline{M(U)}$. $\mathfrak{X}_0$ is evidently a linear subspace of $\mathfrak{X}$. It follows from theorem 1 that $\mathfrak{X}_0 = N_m \oplus \overline{M(U)}$ i. e. every element of $\mathfrak{X}_0$ can be represented in only one manner as the sum $x' + x''$. Since the linear subspace N_m is m-dimensional, there exist m linearly independent linear functionals $f_1, f_2, \ldots, f_m$ defined on N_m. Now put $f_k(x) = f_k(x')$ $(k = 1, 2, \ldots, m)$, where $x \in \mathfrak{X}_0$, $x' \in N_m$. It is easy to see that the functionals f_k are linear on $\mathfrak{X}_0$. Hence, in virtue of the Hahn-Banach theorem ([3], p. 55) these functionals can be linearly extended to the whole space $\mathfrak{X}$. The extended linear functionals f_k $(k = 1, 2, \ldots, m)$ are linearly independent solutions of the adjoint equation, since $f_k(x) = 0$ for $x \in M(U)$.

A particular case of theorem 2 is the following theorem of S. Mazur [1]: *If $\|U\| = 1$, then $p \leqslant q$.*

Theorem 3. *If, in addition to the assumptions in theorem 1, for any x of $\mathfrak{X}$ the sequence $\{C_n(x)\}$, where $C_n(x) = \frac{1}{n} \sum_{k=1}^{n} U^k(x)$ contains a sub-sequence which converges weakly to an element $C(x)$ of $\mathfrak{X}$, then $\mathfrak{X} = N(U) \oplus \overline{M(U)}$.*

Proof. It is easy to see that $x - C_n(x)$ belongs to $M(U)$. But the sequence $\{x - C_n(x)\}$ contains a sub-sequence which converges weakly to $x - C(x)$. Hence we infer that $x - C_n(x)$ belongs to $\overline{M(U)}$. The uniqueness of the representation $x = x' + x''$, where $x' \in N(U)$, $x'' \in \overline{M(U)}$, follows from theorem 1.

From theorem 3 follows

Theorem 4. *Under the same assumptions as in theorem 3, we have $p = q$.*

Proof. By theorem 2 it is sufficient to show that $p \geqslant q$. Let $f_1, f_2, \ldots, f_m$ be linearly independent solutions of the adjoint equation. These linear functionals vanish on $\overline{M(U)}$. By theorem 3 we have $\mathfrak{X} = N(U) \oplus \overline{M(U)}$. Therefore, considering $f_1, f_2, \ldots, f_m$ only on $N(U)$ we establish that these linear functionals are linearly independent. Thus we obtain m linearly independent linear functionals defined on $N(U)$. Hence we infer that there exist in $N(U)$ m linearly independent elements, i. e. m linearly independent solutions of the equation $x - U(x) = 0$.

As an immediate corollary of theorem 4 we obtain the following

Theorem 5. *If $\mathfrak{X}$ is locally weakly compact (i. e. every bounded sequence contains a sub-sequence which converges weakly to an element) and if the conditions of theorem 1 are satisfied, then $p = q$.*

A particular case of theorem 5 is the following theorem of S. Mazur [1]: *if $\mathfrak{X}$ is locally weakly compact and $\|U\| = 1$, then $p = q$.*

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MATHÉMATIQUE

Sur les polynômes en x ne prenant que des valeurs entières pour x entiers

par

A. WAKULICZ

Présenté par W. SIERPIŃSKI à la séance du 14 Décembre 1953

Récemment, W. Sierpiński posa le problème de trouver tous les polynômes en x à coefficients réels qui ne prennent que des valeurs entières pour x entiers. Le but de la présente note est de résoudre ce problème.

Théorème. *Pour qu'un polynôme en x du degré n (où n est un nombre naturel) prenne une valeur entière pour tout nombre entier x, il faut et il suffit qu'il ait la forme*

$$a_0\binom{x}{n} + a_1\binom{x}{n-1} + \ldots + a_{n-1}\binom{x}{1} + a_n, \tag{1}$$

où $a_0, a_1, \ldots, a_n$ sont des nombres entiers.

Ce théorème se déduit immédiatement des lemmes 1 et 2, que nous allons établir à présent.

Lemme 1. *Tout polynôme $f(x)$ en x, du degré n, à coefficients réels, peut être présenté uniquement sous la forme*

$$f(x) = a_0\binom{x}{n} + a_1\binom{x}{n-1} + \ldots + a^n, \tag{2}$$

où $a_0, a_1, \ldots, a_n$ sont des nombres réels.

Démonstration. Déterminons les nombres $a_n, a_{n-1}, \ldots, a_0$ des équations linéaires successives

$$f(k) = a_{n-k}\binom{k}{k} + a_{n-k+1}\binom{k}{k-1} + \ldots + a_{n-1}\binom{k}{1} + a_n, \quad \text{pour} \quad k = 0, 1, \ldots, n \tag{3}$$

et posons

$$g(x) = a_0\binom{x}{n} + a_1\binom{x}{n-1} + \ldots + a_{n-1}\binom{x}{1} + a_n. \tag{4}$$

On a $f(x) = g(x)$ pour $n+1$, valeurs distinctes de la variable x, d'où l'on conclut que les polynômes $f(x)$ et $g(x)$ (du degré n) sont identiques. D'après (4) on a donc la formule (2) pour x réels. D'autre part, ayant la formule (2)

pour x réels, on en déduit les égalités (3) qui déterminent les nombres $a_n, a_{n-1}, \ldots, a_1, a_0$, c. q. f. d.

Lemme 2. *Pour qu'un polynôme $f(x)$ du degré n (où n est un nombre naturel) prenne des valeurs entières pour tout nombre entier x, il faut et il suffit qu'il prenne des valeurs entières pour $n+1$, valeurs entières successives de x *), $x = n_0, n_0+1, \ldots, n_0+n$. Dans ce cas tous les coefficients, $a_0, a_1, \ldots, a_n$ de la forme* (1) *sont entiers.*

Démonstration. La nécessité de cette condition pour tout n naturel est évidente.

Il est facile d'établir la suffisance pour $n=1$. En effet, si $f(x) = a_0\binom{x}{1} + a_1$ et si les nombres $f(n_0)$, $f(n_0+1)$ sont entiers, les nombres $a_0 = f(n_0+1) - f(n_0)$ et $a_1 = f(n_0) - a_0\binom{n_0}{1}$ le sont également. Toutes les valeurs de $f(x)$ sont alors entières pour x entiers.

Supposons le lemme vrai pour $n=k$ et soit $f(x)$ un polynôme du degré $k+1$ qui prend des valeurs entières pour $k+2$ (valeurs entières successives de x, $x = n_0, n_0+1, \ldots, n_0+k+1$); alors

$$f(x) = a_0\binom{x}{k+1} + a_1\binom{x}{k} + \ldots + a_k\binom{x}{1} + a_{k+1}$$

et

$$h(x) = f(x+1) - f(x) = a_0\binom{x}{k} + a_1\binom{x}{k-1} + \ldots + a_k$$

est un polynôme du degré k prenant des valeurs entières pour $k+1$ valeurs entières successives de x, $x = n_0, n_0+1, \ldots, n_0+k$. Les coefficients $a_0, a_1, \ldots, a_k$ sont alors entiers et comme

$$a_{k+1} = f(n_0) - \left[a_0\binom{n_0}{k+1} + a_1\binom{n_0}{k} + \ldots + a_k\binom{n_0}{1}\right],$$

a_{k+1} est aussi entier.

Le lemme est donc démontré par induction.

Corollaire. *La condition nécessaire et suffisante pour que toutes les valeurs d'un polynôme du degré n soient — poux x entiers — entières et divisibles par un entier m, est que tous les coefficients, $a_0, a_1, \ldots, a_n$, de la forme* (1) *du polynôme soient divisibles par m* [1].

La suffisance de la condition suit de la forme (1).

Il est facile d'établir la nécessité pour $n=1$.

En effet, si $f(x) = a_0\binom{x}{1} + a_1$ est un polynôme ne prenant que des valeurs entières divisibles par m pour x entiers, $a_0 = f(x+1) - f(x)$ est divisible par m et $a_1 = f(x) - a_0\binom{x}{1}$ l'est aussi pour x entiers. La démonstration par induction pour un n quelconque ne présente aucune difficulté.

R. D. James [2] a établi les conditions nécessaires et suffisantes pour qu'un polynôme du degré 3 ne prenne que des valeurs entières pour x entiers $\geqslant 0$. Il suit immédiatement du lemme 2 que la forme (1) où

*) Il serait intéressant d'établir sous quelles conditions pour l'ensemble de valeurs entières de x, $x = k_1, k_2, \ldots, k_{n-1}$ ce lemme reste vrai.

$a_0, a_1, \ldots, a_n$ sont entiers, est une telle condition pour n naturel quelconque.

Enfin, il est à remarquer que L. E. Dickson [3] s'est occuppé du problème de déterminer tous les polynômes du degré 2 qui ne prennent que des valeurs entières $\geqslant 0$ pour x entiers $\geqslant 0$.

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MATHÉMATIQUE

Sur une propriété asymptotique des intégrales d'une équation différentielle du second ordre

par

Z. MIKOŁAJSKA

Présenté par T. WAŻEWSKI le 15 Décembre 1953

Envisageons l'équation différentielle

$$\frac{d}{dt}f\left(t,x,\frac{dx}{dt}\right)=g\left(t,x,\frac{dx}{dt}\right). \tag{1}$$

Appelons une fonction $F(t,x,y)$ *inverse* à la fonction $f(t,x,z)$ par rapport à z lorsque les équations $y=f(t,x,z)$ et $z=F(t,x,y)$ sont équivalentes.

Théorème. *Admettons les hypothèses suivantes:*

1° *l'existence de la fonction* $F(t,x,y)$ *inverse à* $f(t,x,z)$ *par rapport à* z,

2° *la continuité des fonctions* $g(t,x,y)$ *et* $F(t,x,y)$ *pour* $t\geqslant 0$ *et* x,y *quelconques,*

3° *l'existence des fonctions* $a(t)$ *et* $b(t)$ *continues pour* $t\geqslant 0$, *telles que* $a(t)>0$, $b(t)\not\equiv 0$, $b(t)\geqslant 0$ *pour* $t\geqslant 0$, $\int_0^\infty a(t)\int_0^t b(s)\,ds\,dt<\infty$ *et satisfaisant aux conditions*

$$|F(t,x,y)|\leqslant|y|\,a(t),\qquad |g(t,x,F(t,x,y))|\leqslant|x|\,b(t)\ ^*),$$

4° *l'unicité des intégrales de l'équation* (1) *pour le problème initial* $x(t_0)=x_0$, $x'(t_0)=p_0$.

Il existe alors, pour tout nombre c, *une famille d'intégrales* $x(t)$ *définies dans un intervalle* $t_0<t\leqslant\infty$ *et telles que*

$$\lim_{t\to\infty}x(t)=c, \tag{2}$$

cette famille dépendant au moins d'un paramètre.

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*) On peut évidemment remplacer la dernière condition par la condition plus simple $|g(t,x,y)|\leqslant|x|b(t)$, qui est moins générale.

Ce théorème est une généralisation aux équations non-linéaires d'un théorème de Wintner [1] sur l'équation linéaire

$$\frac{d}{dt}\left\{p(t)\frac{dx}{dt}\right\} = q(t)x.$$

La démonstration qui suit repose sur une méthode topologique due à Ważewski [2].

Démonstration. La substitution $y = f(t, x, dx/dt)$ appliquée à l'équation (1) donne le système de deux équations

$$(1') \qquad \frac{dx}{dt} = F(t, x, y), \qquad \frac{dy}{dt} = g(t, x, F(t, x, y)).$$

Considérons d'abord le cas où $c \neq 0$. Posons

$$A(t) = \int_t^\infty a(s) \int_0^s b(u)\,du\,ds, \qquad B(t) = \int_0^t b(s)\,ds$$

et choisissons un nombre T de façon à avoir

$$0 < A(t) < \tfrac{1}{3} \quad \text{et} \quad 0 < B(t) \quad \text{pour} \quad t \geqslant T.$$

On montre facilement que

$$(3) \qquad \lim_{t\to\infty} A(t) = 0.$$

Soit ω l'ensemble de tous les points (t, x, y) tels que

$$(4) \qquad |x - c| \leqslant 3|c|A(t) \quad \text{et} \quad |y| \leqslant 2|c|B(t) \quad \text{pour} \quad t \geqslant T.$$

La frontière G de ω, relative au demi-espace $t \geqslant T$, se compose de quatre ensembles S_1, S_2, E_1 et E_2 définis respectivement par les conditions

$$(S_1) \qquad x = 3|c|A(t) + c \quad \text{et} \quad |y| \leqslant 2|c|B(t),$$
$$(S_2) \qquad x = c - 3|c|A(t) \quad \text{et} \quad |y| \leqslant 2|c|B(t),$$
$$(E_1) \qquad |x - c| \leqslant 3|c|A(t) \quad \text{et} \quad y = 2|c|B(t),$$
$$(E_2) \qquad |x - c| \leqslant 3|c|A(t) \quad \text{et} \quad y = -2|c|B(t)$$

pour $t \geqslant T$. Nous allons montrer que l'ensemble

$$S = S_1 + S_2 - E_1 - E_2$$

est celui de tous les points par lesquels les intégrales du système d'équations (1') sortent de ω et que ce sont exclusivement des points de sortie stricte (cf. [2]). Calculons à cet effet la dérivée de la fonction $y - 2|c|B(t)$ le long d'une intégrale quelconque du système d'équations (1') issue d'un point de E_1 et déterminons le signe de cette dérivée aux points appartenant à E_1.

En désignant cette dérivée par $\frac{d}{dt}\{y-2|c|B(t)\}_{(1')}$ nous avons

$$\frac{d}{dt}\{y-2|c|B(t)\}_{(1')}=y'-2|c|b(t)\leqslant b(t)(|x|-2|c|)\leqslant b(t)|c|(3A(t)-1)<0$$
pour $(t,x,y)\in E_1$

et d'une façon analogue

$$\frac{d}{dt}\{y+2|c|B(t)\}_{(1')}=y'+2|c|b(t)\geqslant b(t)|c|(1-3A(t))>0 \quad \text{pour} \quad (t,x,y)\in E_2,$$

$$\frac{d}{dt}\{x-c-3|c|A(t)\}_{(1')}=F(t,x,y)+3|c|a(t)B(t)\geqslant a(t)|c\ B(t)(3-2)>0$$
pour $(t,x,y)\in S_1$,

$$\frac{d}{dt}\{c-x-3|c|A(t)\}_{(1')}=-x'-3|c|A'(t)\geqslant|c|a(t)\cdot B(t)\cdot(3-2)>0$$
pour $(t,x,y)\in S_2$.

Il résulte de ces quatre inégalités que tous les points de S sont ceux de sortie stricte situés sur G, tandis que les points de $E_1+E_2-S_1-S_2$ sont soit ceux d'entrée stricte, soit ceux de glissement extérieur des intégrales du système d'équations (1'). Posons

$$|y_0|<2|c|B(T) \tag{5}$$

et désignons par $Z(y_0)$ le segment

$$t=T \qquad y=y_0, \qquad |x-c|\leqslant 3|c|A(T).$$

L'ensemble $S\cdot Z(y_0)$ se réduit aux deux extrémités du segment $Z(y_0)$ et par conséquent il n'en est pas un rétracte. Mais il est facile de vérifier que $S\cdot Z(y_0)$ est un rétracte de S. On en conclut en vertu du théorème de Ważewski, établi dans son travail précité, que $Z(y_0)$ contient au moins un point P qui est le point d'issue d'une intégrale de (1') définie dans l'intervalle $T\leqslant t<\infty$ et parcourant dans ω quand t parcourt cet intervalle. Il s'ensuit de (3) et (4) que l'intégrale en question satisfait à (2). Enfin, les segments $Z(y_0)$ étant par définition disjoints pour tout couple de valeurs distinctes prises par y_0 et assujetties à (5), la famille des intégrales en question dépend en effet d'un paramètre au moins (cf. [3]).

Quant au cas où $c=0$, le raisonnement est analogue. La condition (4), qui définit l'ensemble ω, est alors à remplacer par la suivante:

$$|x|\leqslant 2A(t) \quad \text{et} \quad |y|\leqslant B(t) \quad \text{pour} \quad t\geqslant T.$$

Remarque 1. On parvient à un résultat analogue pour le système d'équations de la forme

$$x'=h(t,x,y), \qquad y'=k(t,x,y),$$

traité indépendamment de l'équation du second ordre de la forme (1).

Remarque 2. En appliquant le théorème qui vient d'être établi à l'équation linéaire traitée par Wintner [1], on conclut immédiatement qu'il existe deux intégrales linéairement indépendantes dont chacune tend à une limite finie pour $t\to\infty$. Il en résulte que chaque intégrale de cette équation tend à une limite finie.

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MATHÉMATIQUE

Un théorème sur l'uniformisation des fonctions continues et son application à la démonstration du théorème de F. J. Dyson sur les transformations de la surface sphérique

par

K. ZARANKIEWICZ

Présenté par K. KURATOWSKI à la séance du 30 Décembre 1953

1. Théorème. *Soit* $f_i(x)$, *où* $0 \leqslant x \leqslant 1$ *et* $i = 1,2,\ldots,m$, *un système de m fonctions continues satisfaisant aux deux conditions suivantes:*

(1) $$\alpha = f_i(0) \leqslant f_i(x) \leqslant f_i(1) = \beta \quad \text{pour} \quad i = 1,2,\ldots,m,$$

(2) *l'intervalle* 0 1 *se laisse subdiviser en un nombre fini d'intervalles dans lesquels chacune des fonctions* $f_i(x)$ *est monotone.*

Dans ces conditions, il existe un système de m fonctions continues $g_i(t)$ *où* $0 \leqslant t \leqslant 1$ *et* $i = 1,2,\ldots,m$, *telles qu'on a pour tout t:*

(3) $$0 = g_i(0) \leqslant g_i(t) \leqslant g_i(1) = 1,$$

(4) $$f_1 g_1(t) = f_2 g_2(t) = \ldots = f_m g_m(t).$$

La démonstration de ce théorème paraitra dans Fundamenta Mathematicae. Ajoutons que, pour les buts de la note présente, il suffit d'établir ce théorème dans le cas particulier où $m = 2$ et où le terme "monotone" dans la condition (2) est remplacé par "linéaire".

2. Désignons par S_n $(n > 1)$ la surface de la sphère à $n+1$ dimensions, de centre 0 et de rayon 1. Pour $X \subset S_n$, désignons par X^* l'ensemble antipode de X, c. à. d. l'ensemble des points $p^* = (-p)$ où $p \in X$. Nous appelerons antipodique tout ensemble X vérifiant la condition $X^* = X$.

Lemme de Kuratowski. *F étant un ensemble antipodique fermé, composé d'un nombre fini de composantes*), ou bien F, ou bien le complémentaire de F (c. à. d. l'ensemble* $S_n - F$) *contient une composante antipodique.*

Soit, en effet, C une composante non antipodique de $S_n - F$. Elle contient donc un point p dont l'antipode p^* ne lui appartient pas. Comme

*) Par composante d'un ensemble A on entend un sous-ensemble connexe de A qui n'est contenu dans aucun autre sous-ensemble connexe de A.

antipodique, l'ensemble $S_n - F$ contient le point p^*. L'ensemble F sépare *) donc l'espace S_n entre les points p et p^*. Il contient, par conséquent **), une composante qui sépare S_n entre ces deux points; soient $K_1, K_2, \ldots, K_m$ toutes les composantes de ce genre. D'après un théorème général ([2], p. 98 et [3]), étant donnés dans un espace connexe, deux points p et q et une famille (finie) d'ensembles connexes fermés et disjoints, qui séparent l'espace entre p et q, on peut numéroter ces ensembles de façon que chacun d'eux sépare l'espace entre la somme des ensembles qui le précèdent (augmentée du point p) et celle de tous les ensembles qui le suivent (augmentée du point q). Admettons donc que les ensembles $K_1, K_2, \ldots, K_m$ soient numérotés de cette façon. L'ensemble F étant antipodique, les ensembles $K_1^*, K_2^*, \ldots, K_m^*$ sont également des composantes de F et séparent S_n entre p^* et p. On constate aussitôt que

$$K_1^* = K_m, \qquad K_2^* = K_{m-1}, \qquad \ldots, \qquad K_m^* = K_1.$$

Dans le cas où $m = 2j - 1$, il vient $K_j^* = K_j$, et la composante K_j est antipodique.

Admettons donc que m soit pair: $m = 2j$. Il vient $K_j^* = K_{j+1}$.

Nous allons montrer qu'il existe une composante D de $S_n - F$ telle que

$$\overline{D} \cdot K_j \neq 0 \neq \overline{D} \cdot K_j^*. \tag{5}$$

Unissons à ce but les points p et p^* par un arc L en dehors de l'ensemble $Z = F - (K_1 + K_2 + \ldots + K_m)$. Un tel arc existe, car aucune composante de l'ensemble Z n'étant une coupure entre p et p^*, Z n'est non plus une coupure entre ces points ([2], p. 334, 3). D'autre part, les ensembles K_j et K_j^* étant des coupures entre p et p^*, on a $L \cdot K_j \neq 0 \neq L \cdot K_j^*$.

Extrayons de L un arc qr irréductible entre K_j et K_j^*, c'est-à-dire tel que

$$qr \cdot K_j = (q), \qquad qr \cdot K_j^* = (r). \tag{6}$$

Nous en déduirons que

$$(qr - q - r) \cdot F = 0. \tag{7}$$

En effet, dans le cas contraire, il existerait un point u et un indice i tels que $u \in qr \cdot K_i$ et $j \neq i \neq j+1$.

En supposant que $i < j$, l'arc ur unirait les ensembles K_j et K_{j+1} et — comme K_j sépare l'espace entre ces ensembles — on aurait $ur \cdot K_j \neq 0$, contrairement à (6). Le cas où $i > j+1$ est analogue.

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*) On dit qu'un ensemble fermé F sépare l'espace X entre deux ensembles P et Q lorsque l'ensemble $X - F$ se décompose en deux ensembles ouverts disjoints dont l'un contient P et l'autre Q.

**) C'est une conséquence de l'unicohérence de l'espace S_n ([2], p. 333, 9,2°, p. 335, 1 et p. 336, 3). Rappelons qu'un espace connexe X est dit unicohérent, lorsque pour toute décomposition $X = A + B$ en deux ensembles connexes fermés, le produit $A \cdot B$ est connexe.

La formule (7) établie, on en déduit l'existence d'une composante D de $S_n - F$ qui contient l'ensemble connexe $qr - q - r$. Il vient $q \in \overline{D}$ et $r \in \overline{D}$, d'où la formule (5). Elle implique aussitôt que

$$\overline{D^*} \cdot K_j^* \neq 0 \neq \overline{D^*} \cdot K_j, \tag{8}$$

c'est-à-dire que les deux composantes D et D^* de l'ensemble $S_n - F$ satisfont à la même formule (5). Nous en déduirons que

$$D^* = D, \tag{9}$$

ce qui terminera la démonstration du lemme.

Or, remarquons d'abord que l'ensemble $S_n - D$ n'est pas connexe entre K_j et K_j^*, c'est-à-dire qu'il existe deux ensembles fermés A et B tels que:

$$S_n - D = A + B, \qquad A \cdot B = 0, \tag{10}$$

$$K_j \subset A, \qquad K_j^* \subset B. \tag{11}$$

Posons, en effet, conformément à (5): $a \in \overline{D} \cdot K_j$ et $b \in \overline{D} \cdot K_j^*$. En supposant que l'ensemble $S_n - D$ soit connexe entre K_j et K_j^*, il le serait également entre a et b. Comme, d'autre part, $\overline{D}$ est aussi connexe entre ces points, il en résulte en vertu de l'unicohérence de l'espace S_n, que le produit $(S_n - D)\overline{D} = \mathrm{Fr}(D)$ est connexe entre a et b ([2], p. 334, 3). Mais cela est impossible, car la frontière de D est sous-ensemble de F, qui n'est pas connexe entre K_j et K_j^* (donc entre a et b).

L'existence des ensembles fermés A et B satisfaisant aux conditions (10) et (11) étant établie, supposons par impossible que l'identité (9) soit en défaut, donc que $D \cdot D^* = 0$. Il en résulte en vertu de (10) que $D^* \subset A + B$, et comme $A \cdot B = 0$, on a $D^* \subset A$ ou bien $D^* \subset B$. En admettant que $D^* \subset A$, il vient $\overline{D^*} \subset A$, donc $\overline{D^*} \cdot B = 0$, d'où en vertu de (11), $\overline{D^*} \cdot K_j^* = 0$, contrairement à (8). Le cas où $D^* \subset B$ est analogue.

Remarque. La démonstration qui précède est applicable au cas plus général où l'on remplace S_n par un continu localement connexe unicohérent et où l'on entend par transformation antipodique une *involution* continue arbitraire. Ajoutons qu'en complétant de façon convenable la démonstration, on peut omettre l'hypothèse que le nombre de composantes de F soit fini.

3. Théorème de Dyson. *Soit f une fonction continue à valeurs réelles définie sur la surface sphérique S_2. À tout nombre d tel que $0 < d < 2$ correspond un rectangle (inscrit dans S_2) abb^*a^* tel que*

$$|a - b| = d, \qquad f(a) = f(b) = f(b^*) = f(a^*). \tag{12}$$

Démonstration. Toute transformation continue de S_2 se laissant approcher par des transformations simpliciales, le théorème se réduit au cas où f en est une; cela veut dire que S_2 est représentée dans une décomposition simpliciale et sur tout simplexe de cette décomposition la fonction f est linéaire. Désignons par F l'ensemble de tous les points p de S_2 tels que

$f(p) = f(p^*)$. Évidemment, F est un polyèdre antipodique. En outre, aucune composante R de $S_2 - F$ n'est antipodique. Soit, en effet, $p_0 \in R$. On a donc, soit $f(p_0) > f(p_0^*)$, soit $f(p_0) < f(p_0^*)$. Admettons la première inégalité. On a alors, en vertu de la connexité de R, $f(p) > f(p^*)$ pour tout point p de R. Cependant, en supposant que R est antipodique, cette inégalité n'est pas satisfaite par $p = p_0^* \in R$ car $f(p_0^*) < f(p_0) = f(p_0^{**})$. Ayant ainsi établi que l'ensemble $S_2 - F$ ne contient aucune composante antipodique, nous concluons du lemme que F en contient une; désignons la par C.

Désignons par α et β les bornes, inférieure et supérieure, de la fonction f, son argument p parcourant C. Soient: $f(p) = \alpha$ et $f(q) = \beta$. Comme $C = C^*$, on a $q^* \in C$. Soient pq et pq^* deux lignes brisées (sphériques) contenues dans C. Envisageons leurs représentations paramétriques $h_1(x)$ et $h_2(x)$ sur l'intervalle $0 \leqslant x \leqslant 1$; de façon plus précise: les fonctions h_1 et h_2 transforment l'intervalle 01 en pq et pq^* respectivement, on a

$$h_1(0) = p = h_2(0), \qquad h_1(1) = q, \qquad h_2(1) = q^* \tag{13}$$

et, de plus, l'intervalle 01 se laisse subdiviser en un nombre fini d'intervalles dans lesquels les fonctions h_1 et h_2 sont linéaires. En posant

$$f_i(x) = f h_i(x) \quad \text{pour} \quad i = 1, 2, \tag{14}$$

on constate aussitôt que les hypothèses du théorème du N° 1 sont réalisées Envisageons les fonctions $g_1(t)$ et $g_2(t)$ satisfaisant aux conditions (3) et (4) et posons

$$\varrho(t) = |h_1 g_1(t) - h_2 g_2(t)|. \tag{15}$$

D'après (3), (13) et (15) il vient $\varrho(0) = 0$ et $\varrho(1) = |q - q^*| = 2$. Comme $0 < d < 2$, il existe un t_0 tel que $\varrho(t_0) = d$. Posons

$$a = h_1 g_1(t_0) \quad \text{et} \quad b = h_2 g_2(t_0). \tag{16}$$

Le rectangle à sommets: a, b, a^* et b^*, est le rectangle demandé. Car d'après (15) et (16) on a $|a - b| = \varrho(t_0) = d$ et le reste de la condition (12) résulte des formules (4), (14) et (16), puisque $a, b \in F$.

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MATHEMATICS

Constructive Theories

by

H. RASIOWA

Presented by K. KURATOWSKI on December 31, 1953

Let $\mathcal{T}(\mathfrak{A})$ be an axiomatic theory (with a set $\mathfrak{A}$ of axioms) formalized on the basis of the *intuitionistic functional calculus* ([3], [7], p. 84) of the first order. We assume that the following symbols are the primitive signs of $\mathcal{T}(\mathfrak{A})$: *individual variables* $x_1, x_2, \ldots$; *individual constants* $x_0, x_{-1}, x_{-2}, \ldots$; *functors with l arguments* $f_1^l, f_2^l, \ldots$ (i. e. symbols for functions from individuals to individuals); *predicates with k arguments* $F_1^k, F_2^k, \ldots$ (i. e. symbols for relations); *sentential operators* $+, \cdot, \rightarrow, \neg$; *quantifiers* $\sum_{x_i}, \prod_{x_i}$ $(i = 1, 2, \ldots)$. The set of individual constants and the set of functors may be either infinite or finite, or empty. The set of predicates may be also infinite or finite. We assume, however, that it contains at least one element. The predicate F_1^2 will play the role of the *sign of equality*, i. e. if F_1^2 occurs among the primitive symbols of $\mathcal{T}(\mathfrak{A})$, then the set $\mathfrak{A}$ of axioms of $\mathcal{T}(\mathfrak{A})$ contains the axioms of equality *). We suppose that all axioms of $\mathcal{T}(\mathfrak{A})$ are *closed* **) formulas.

We assume the known rules of inference of the intuitionistic functional calculus. The *theorems* of $\mathcal{T}(\mathfrak{A})$ are all $\alpha \in \mathfrak{A}$, all substitutions of theorems of the intuitionistic sentential calculus and all their consequences.

A theory $\mathcal{T}(\mathfrak{A})$ is said to be *constructive* provided that 1° if $\sum_{x_p} \alpha$ is a theorem in $\mathcal{T}(\mathfrak{A})$, then there exists a term ξ ***) such that the formula

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*) The axioms of equality in our notation have the following form: $\Pi_{x_1} F_1^2(x_1, x_1)$; $\Xi\left(F_1^2(x_1, x_2) \rightarrow \left(\alpha \rightarrow \alpha\binom{x_2}{x_1}\right)\right)$, where $\alpha\binom{x_2}{x_1}$ results from α by the admissible substitution of x_2 for x_1 and Ξ is written instead of the quantifiers Π_{x_j} bounding all free occurences of individual variables in the next formula. See [4], p. 33.

**) A formula is closed if it contains no free occurences of individual variables.

***) Individual variables and constants are terms. If $\xi_1, \ldots, \xi_l$ are terms, then so is $f_n^l(\xi_1, \ldots, \xi_l)$.

$\alpha(x_p^{\xi})$ which results from α by the substitution *) of ξ for x_p is a theorem in $\mathcal{T}(\mathfrak{A})$;

2^0 if $\alpha+\beta$ is a theorem in $\mathcal{T}(\mathfrak{A})$, then either α or β is a theorem in $\mathcal{T}(\mathfrak{A})$.

We shall formulate a necessary and sufficient condition for a theory $\mathcal{T}(\mathfrak{A})$ to be constructive. This condition has a purely algebraic form. In order to formulate the condition in question we need several difinitions.

Given a formula α of $\mathcal{T}(\mathfrak{A})$, let $|\alpha|$ denote the class of all formulas β of $\mathcal{T}(\mathfrak{A})$ such that $\alpha\to\beta$ and $\beta\to\alpha$ are theorems of $\mathcal{T}(\mathfrak{A})$. Let $L(\mathfrak{A})$ **) be the algebra of all cosets $|\alpha$ (where α is a formula of $\mathcal{T}(\mathfrak{A})$ with operations:

$$|\alpha|+|\beta|=|\alpha+\beta|,\quad |\alpha|\cdot|\beta|=|\alpha\cdot\beta|,\quad |\alpha|\to|\beta|=|\alpha\to\beta|,\quad \neg|\alpha|=|\neg\alpha|.$$

$L(\mathfrak{A})$ is a pseudocomplemented lattice ([1] p. 147) with the unit element $e=|\alpha|$ where α is a theorem of $\mathcal{T}(\mathfrak{A})$. Given a formula α of $\mathcal{T}(\mathfrak{A})$ we have

$$(*)\quad \sum_{\xi\in J}|\alpha(x_l^{\xi})|=\Big|\sum_{x_l}\alpha\Big|,\qquad (**)\quad \prod_{\xi\in J}|\alpha(x_l^{\xi})|=\Big|\prod_{x_l}\alpha\Big|,$$

where J is the set of all terms of $\mathcal{T}(\mathfrak{A})$.

It is proved in [7] (11.2, p. 86) that there exists an isomorphism h of $L(\mathfrak{A})$ into an algebra $\boldsymbol{H}(\mathfrak{X})$ of all open subsets of some topological space $\mathfrak{X}$ [5] preserving sums (*) and products (**). The algebraic operations in $\boldsymbol{H}(\mathfrak{X})$ are defined as follows: $+$ and $\cdot$ are the set-theoretical operations of sum and of product, $a\to b=\mathrm{Int}(-a+b)$, $\neg a=\mathrm{Int}(-a)$.

Let x be a fixed element, such that x non $\epsilon\,\mathfrak{X}$ and let $\mathfrak{X}^0=\mathfrak{X}+(x)$. We shall conceive the set $\mathfrak{X}^0$ as a topological space with the following definition of the topology ***): the open subsets of $\mathfrak{X}^0$ are open subsets of $\mathfrak{X}$ and the whole space $\mathfrak{X}^0$.

Each formula α of $\mathcal{T}(\mathfrak{A})$ will be treated as an algebraic functional Φ_α ([7], p. 71) defined in the domain J of all terms of $\mathcal{T}(\mathfrak{A})$ with the values in $\boldsymbol{H}(\mathfrak{X}^0)$ by considering: the individual variables (constants) x_l as variables j_l running over J (as the fixed elements j_l of J), f_n^l — as l-argument functions from term to term, F_m^k — as k-argument functions defined on J with values belonging to $\boldsymbol{H}(\mathfrak{X}^0)$, the logical signs $+$, $\cdot$, $\to$, $\neg$ — as the corresponding algebraical operations in $\boldsymbol{H}(\mathfrak{X}^0)$, the quantifiers $\sum\limits_{x_p}$ and $\prod\limits_{x_p}$ — as the signs of infinite sums $\boldsymbol{H}(\mathfrak{X}^0)\sum\limits_{x_p\in J}$ and products $\boldsymbol{H}(\mathfrak{X}^0)\prod\limits_{x_p\in J}$ respectively.

Let Ψ_α denote the value of Φ_α for the following valuation of its arguments:

1^0 the value of x_l is $x_l\,\epsilon\,J$,

*) We assume that the necessary changes in the bound variables of α have been performed, before the operation of substitution has been applied.

**) We apply the known construction of Lindenbaum. Cf. for instance [7], p. 69.

***) This construction was applied in [8], and is due to McKinsey and Tarski [6].

2^0 the value of f_n^l is the function by which the term $f_n^l(\xi_1, \ldots, \xi_l)$ corresponds to the terms $\xi_1, \ldots, \xi_l$,

3^0 the value of F_m^k is the function φ_m^k defined as follows: given any terms $\xi_1, \ldots, \xi_k$

$$\varphi_m^k(\xi_1, \ldots, \xi_k) = \begin{cases} \mathfrak{X}^0 & \text{if } |F_m^k(\xi_1, \ldots, \xi_k)| = e \\ h|F_m^k(\xi_1, \ldots, \xi_k)| & \text{in the case of } |F_m^k(\xi_1, \ldots, \xi_k)| \neq e. \end{cases}$$

Theorem I. *A theory* $\mathcal{T}(\mathfrak{A})$ *is constructive if and only if* $\Psi_\alpha = \mathfrak{X}^0$ *for every axiom* α *of* $\mathcal{T}(\mathfrak{A})$.

Theorem II. *The axioms of equality are constructive* *).

Given a theory $\mathcal{T}(\mathfrak{A})$, let $\mathcal{Z}(\mathfrak{A})$ be always the least set of formulas of $\mathcal{T}(\mathfrak{A})$ satisfying the following conditions: 1^0 $\mathcal{Z}(\mathfrak{A})$ contains all elementary formulas $F_m^k(\xi_1, \ldots, \xi_k)$ of $\mathcal{T}(\mathfrak{A})$, 2^0 if $\beta, \gamma \in \mathcal{Z}(\mathfrak{A})$, then $\beta \cdot \gamma \in \mathcal{Z}(\mathfrak{A})$, 3^0 if $\gamma \in \mathcal{Z}(\mathfrak{A})$ then $\beta \to \gamma, \neg\gamma, \prod\limits_{x_p} \gamma \in \mathcal{Z}(\mathfrak{A})$.

Theorem III. *If the axioms of a theory* $\mathcal{T}(\mathfrak{A})$ *(except the axioms of equality) belong to the set* $\mathcal{Z}(\mathfrak{A})$, *then* $\mathcal{T}(\mathfrak{A})$ *is constructive theory.*

It follows from III that every theory the axioms of which are equalities is constructive. For example the theories of groups, of fields and of lattices are constructive. More generally, if we remove the sign of the alternative and the existential quantifiers from the axioms of a theory $\mathcal{T}(\mathfrak{A})$ (which do not belong to $\mathcal{Z}(\mathfrak{A})$), using de Morgan's laws, we obtain a weaker theory, which is constructive. In this way one can obtain a constructive fragment of arithmetic.

Theorem IV. *Let* $\mathcal{T}(\mathfrak{A})$ *be a constructive theory and let* β *be an arbitrary formula of this theory of the form*

$$\beta = \overset{(1)}{\underset{x_{p_1}}{\Xi}} \ldots \overset{(n)}{\underset{x_{p_n}}{\Xi}} \alpha$$

where α *contains no quantifiers and* $\overset{i}{\Xi}$ *is either the sign* $\sum$ *or* $\prod (i = 1, \ldots, n)$. *Then there exists a sequence* $\alpha_1, \alpha_2, \ldots$ *of formulas without quantifiers such that* β *is a theorem of* $\mathcal{T}(\mathfrak{A})$ *if and only if at least one of the formulas* $\alpha_1, \alpha_2, \ldots$ *is a theorem of* $\mathcal{T}(\mathfrak{A})$. *If a theory* $\mathcal{T}(\mathfrak{A})$ *contains no functors and the set of individual constants is finite then the sequence of formulas* $\alpha_1, \alpha_2, \ldots$ *reduces to the finite sequence.*

This theorem may be considered as an analogue of Herbrand's theorem [2].

Let α be an arbitrary closed formula of the functional calculus of Heyting. Such a formula can be treated as the single axiom of a theory $\mathcal{T}((\alpha))$. If $\mathcal{T}_{\backslash}((\alpha))$ is constructive, we shall say that α is a *constructive* formula.

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*) More precisely, if a theory $\mathcal{T}(\mathfrak{A})$ contains the set $\mathfrak{E}$ of axioms of equality, then for every $\alpha \in \mathfrak{E}$, $\Psi_\alpha = \mathfrak{X}^0$.

Theorem V. *If α is a constructive closed formula, then for every formula β, $\alpha \to \sum_{x_p} \beta$ is provable in the functional calculus of Heyting if and only if there exists x_q such that the formula $\alpha \to \beta\binom{x_q}{x_p}$ is provable.*

Theorem VI. *If α is a constructive closed formula of the functional calculus of Heyting, then for every formula β of the form $\beta = \overset{(1)}{\underset{x_{p_1}}{\Xi}} \ldots \overset{(n)}{\underset{x_{p_n}}{\Xi}} \gamma$ where γ contains no quantifiers and $\overset{(i)}{\Xi}$ is either the sign $\sum$ or $\prod$, there exists a finite sequence $\gamma_1, \ldots, \gamma_m$ of formulas without quantifiers such that $\alpha \to \beta$ is provable if and only if at least one of the formulas $\alpha \to \gamma_1, \ldots, \alpha \to \gamma_m$ is provable.*

Theorem V is stronger than the fundamental theorem (χ) of [8].

The proofs of theorems I—VI will be given in the paper *Algebraic Models of Axiomatic Theories*, Fundamenta Mathematicae 41 (1954).

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[1]) Cf. [2].

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MATHEMATICS

On a Problem of Sierpiński Concerning Congruent Sets of Points

by

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Communicated by W. SIERPIŃSKI on January 11, 1954

Professor W. Sierpiński has proposed the following problem:

Does there exist in the plane or in three-dimensional space a set of points which is congruent with each subset obtained by taking out of it a single point?

He has given an example of such a set in Hilbert space [1].

In the case of the plane the answer to the above question remains open; in the case of three-dimensional space it is positive, by the following theorems:

Theorem 1. *There exists on the sphere a countable set E such that*

$$E - F \simeq E \text{ *})}$$

for each finite set F.

Theorem 2. *There exists on the sphere a set E of power $\mathfrak{c}$ (power of the continuum) such that*

$$E - D \simeq E$$

for each set D finite or countable.

The proof of theorem 1 is effective, that of theorem 2 non-effective; in neither is the continuum hypothesis assumed **). The proofs are based on the following lemma, proved effectively by Sierpiński [2]:

There exists a free group of rotations of the sphere with a set of generators of power $\mathfrak{c}$.

To obtain theorems 1 and 2, we prove some algebraical lemmas. The lemma for theorem 2 — similar to that for theorem 1 — is:

A free group G with a set M of generators of power $\mathfrak{c}$ contains a set S of power $\mathfrak{c}$ such that for each finite or countable set $Q \subset S$ there exists a ge-

*) The sign $\simeq$ denotes congruence of sets by rotation (reflection excluded).

**) The proofs will be published in Fundamenta Mathematicae.

nerator $\varphi_Q \in M$ *satisfying the condition*

$$\varphi_Q S = S - Q$$

($\varphi_Q S$ denotes the set of all those elements of the group G which are of the form $\varphi_Q \sigma$ where $\sigma \in S$).

The proof of this lemma is essential and is the most difficult step of the proof of theorem 2.

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Nonlinearity of the Polarization of Ferroelectric Titanates in Weak Fields above the Curie Point

by

A. PIEKARA

Communicated by A. SOŁTAN at the meeting of December 14, 1953

According to the Mason-Matthias theory [1], [2], the dipole polarization of $BaTiO_3$-crystals along the c-axis may be expressed in the form

$$p = \frac{\sinh(sp + x)}{\cosh(sp + x) + 2}, \tag{1}$$

where p, x and s are given in the following formulas: the dimensionless polarization

$$p = \frac{P}{n\mu}, \tag{2}$$

where P is the actual polarization, n the number of titanium ions per c. c., and μ the dipole moment of the off-centered Ti ion in the TiO_6 octahedra; the dimensionless external field (E):

$$x = \frac{\mu E}{kT(1 - \frac{4}{3}\pi\gamma)}, \tag{3}$$

where γ is the polarizability of the unit volume without Ti ions contribution; the cooperation factor of the polarized octahedra,

$$s = \frac{n\mu^2\beta}{kT(1 - \frac{4}{3}\pi\gamma)}, \tag{4}$$

where β is the Lorentz factor, different from $4\pi/3$. When $s \leqslant 3$, Eq. (1) for $x = 0$ has the solution $p = 0$ only; this means that spontaneous polarization vanishes when $T \geqslant T_0$, T_0 being the Curie temperature.

Above the Curie point we are dealing with induced polarization only, which is a distinct nonlinear function of the field E, according to Eq. (1).

A peculiar feature of expression (1) was discussed by the author in a recent paper [3], viz. the vanishing of the first order saturation effect. As was shown in this paper, the development of p in a power series above

the Curie point gives

$$p = \sum_{n=1}^{\infty} a_n x^n \tag{5}$$

with the coefficients

$$\begin{aligned} a_1 &= \frac{1}{3-s}, \\ a_2 &= a_3 = a_4 = 0, \\ a_5 &= -\frac{27}{20}\frac{1}{(3-s)^6}. \end{aligned} \tag{6}$$

Consequently, the change in the dielectric constant, $\Delta\varepsilon$, under the influence of the applied electric field, for weak fields should be proportional to x^4

$$\Delta\varepsilon = -27\pi\left(1+\frac{\beta\gamma}{1-\frac{4}{3}\pi\gamma}\right)\frac{s}{\beta}\frac{x^4}{(3-s)^6}. \tag{7}$$

This expression, however, is largely discrepant with that obtained in the experiment for $BaTiO_3$ and (Ba, Sr)TiO_3 (Piekara and Pająk [4]), which for a weak field up to 4 kV./cm. gives:

$$\Delta\varepsilon \sim -E^2. \tag{8}$$

The above expression results also from Roberts' [5] empirical formula relating the measured dielectric constant to the applied field, above the Curie temperature:

$$E = \left(\frac{\alpha}{3}\right)^{3/2}\beta^{-1/2}\left(\frac{\varepsilon_1}{\varepsilon}-1\right)^{1/2}\left(\frac{\varepsilon_1}{\varepsilon}+2\right), \tag{9}$$

where ε_1 is the dielectric constant measured at zero field and α and β are some constants. Eq. (9) gives the increase of the dielectric constant $\Delta\varepsilon = \varepsilon - \varepsilon_1$ for weak fields as:

$$\Delta\varepsilon = -3\beta\varepsilon_1^4 E^2. \tag{10}$$

This expression agrees well with the results of Robert's experiments for fields up to several kV./cm.

Evidently, a correct nonlinear theory must account for the fact of proportionality between $\Delta\varepsilon$ and E^2 for weak fields. According to the author, one of the disadvantages of the Mason-Matthias theory is due to its disregard of the anisotropy of atomic polarizability of titanium ions, which consists in the elastic displacement of titanium ions against the lattice under influence of the electric field. We shall call this polarizability "ion-lattice polarizability" as it is a property of the ion-lattice bond, and not of the ion only. Titanium ion-lattice polarizability is assumed to be anisotropic in this sense that measurement of α along one of the crystallographic axes should yield two

different values: a lower one (α_1) when the titanium ion occupies one of the potential wells (e. g. 1, 2) lying along the direction in question, and a higher one (α_3) if the titanium ion occupies one of the wells (e. g. 3, 4, 5, 6) lying in a plane perpendicular to the direction of the measuring field.

This assumption can be supported by the X-ray analysis, made recently by H. T. Evans, Jr. and published in a paper by A. von Hippel [6]. This analysis shows the thermal amplitudes of titanium ions to be smaller in the displacement direction than in the perpendicular one. Similar behaviour is to be expected when the shift is due to the field, that is why we take $\alpha_3 > \alpha_1$.

In order to get dimensionless units for polarizabilities, the following definitions are introduced:

$$\begin{aligned} \gamma_1 &= \frac{\alpha_1}{\mu^2/kT}, \\ \gamma_3 &= \frac{\alpha_3}{\mu^2/kT}, \\ \gamma_E &= \frac{\alpha_E}{\mu^2/kT}, \\ \gamma_c &= \frac{\gamma/n}{\mu^2/kT}, \end{aligned} \tag{11}$$

where α_E is the electronic polarizability of the titanium ion, γ/n is the total (electronic and ion-lattice) polarizability of all the ions of a unit cell without the titanium ion contribution and μ^2/kT is the dipole polarizability due to the off-centered titatium ion. Thus the relative magnitude of the total polarization defined by Eq. (2) will be:

$$p = [\gamma_c + \gamma_E + \gamma_1 + 4p_3(\gamma_3 - \gamma_1)]X + p_1 - p_2, \tag{12}$$

where p_1, p_2 and p_3 are the probabilities of finding the titanium ion in the potential well 1, 2 and 3-6 respectively; X is a dimensionless expression for the local field F:

$$X = \frac{\mu F}{kT} = \frac{\mu}{kT}\,\frac{E + \beta P_{Ti}}{1 - \frac{4}{3}\pi\gamma} = x + s p_{Ti}. \tag{13}$$

P_{Ti} represents here the total polarization of the titanium ions only and $p_{Ti} = P_{Ti}/n\mu$ is the same polarization expressed in dimensionless units.

Taking into account the anisotropy of the titanium ion-lattice polarizability (i. e. assuming $\gamma_1 \neq \gamma_3$), the energy of the titanium ion can be evaluated and the probabilities p_1, p_2 and p_3 can be calculated by means of Boltzmann's principle. Thus for the total dimensionless polarization we obtain the expression:

$$\begin{aligned} p = \left[\gamma_c + \gamma_E + \gamma_1 + 2(\gamma_3 - \gamma_1)\,\frac{e^{1/2(\gamma_3-\gamma_1)X^2}}{\cosh X + 2\,e^{1/2(\gamma_3-\gamma_1)X^2}}\right] X \\ + \frac{\sinh X}{\cosh X + 2\,e^{1/2(\gamma_3-\gamma_1)X^2}}. \end{aligned} \tag{14}$$

The first term represents the electronic and ion-lattice polarization of the crystal, the second term — the dipole polarization only. This term, when $\gamma_1 = \gamma_3$, becomes Eq. (1) of the Mason-Matthias theory.

For weak fields above the Curie point expression (14) can be expanded in a power series in the form

$$p = \left[\gamma_c + \gamma_E + \frac{1}{3}(\gamma_1 + 2\gamma_3) + \frac{1}{3}\right]\frac{x}{1-\frac{1}{3}S} - \frac{2}{9}(\gamma_c s + 1)(\gamma_3 - \gamma_1)\left(1 - \frac{\gamma_3 - \gamma_1}{2}\right)\frac{x^3}{(1-\frac{1}{3}S)^4} \tag{15}$$

where $S = (1 + \gamma_1 + 2\gamma_3 + 3\gamma_E)s$.

Now, the dielectric constant can be calculated from the relation

$$\varepsilon = \frac{d}{dE}(E + 4\pi P) = 1 + 4\pi\frac{s}{\beta}\frac{dp}{dx}. \tag{16}$$

Thus the change in the dielectric constant, $\Delta\varepsilon = \varepsilon - \varepsilon_1$, due to the application of the field is given by

$$\Delta\varepsilon = -216\pi\frac{s}{\beta}(\gamma_c s + 1)(\gamma_3 - \gamma_1)\left(1 - \frac{\gamma_3 - \gamma_1}{2}\right)\frac{x^2}{(3 - S)^4} \tag{17}$$

or

$$\Delta\varepsilon = -54\frac{(\gamma_3 - \gamma_1)\left(1 - \frac{\gamma_3 - \gamma_1}{2}\right)}{\left[4\pi\frac{s}{\beta}(\gamma_c s + 1)\right]^3}(\varepsilon_1 - \varepsilon_0)^4 x^2, \tag{18}$$

where ε_0 denotes the dielectric constant of the lattice without participation of titanium ions. Since, according Mason and Mathias, $\varepsilon_0 \ll \varepsilon_1$, this expression is in agreement with Roberts' empirical equation (10).

Summarizing, we can say that by taking into account the anisotropy of the titanium ion-lattice polarizability we are enabled to understand the experimental relation $\Delta\varepsilon \sim -E^2$.

For numerical evaluation we may rewrite Eq. (17) using the relation $S \cong \frac{\text{const.}}{T}$ and taking $S = 3$ at the Curie temperature T_0; we find for a temperature range above the Curie point:

$$\Delta\varepsilon = -2\frac{\varepsilon_1 - \varepsilon_0}{\left(\frac{T - T_0}{T}\right)^3}(\gamma_3 - \gamma_1)\left(1 - \frac{\gamma_3 - \gamma_1}{2}\right)x^2. \tag{19}$$

Let us put for $BaTiO_3$ according to Mason [2]: $\mu = 1.56 \cdot 10^{-18}$, $T_0 = 393^\circ$ K and $1/(1 - \frac{4}{3}\pi\gamma) = (\varepsilon_0 + 2)/3 = 30.7$ (the last value is inexact because Mason takes for ε_0 the value of the dielectric constant near 0° K, i. e. $\varepsilon_0 = 90$). Furthermore, if we take the measuring temperature $T = 403^\circ$ K, i. e. 10° C. above the Curie point, we obtain, according to Mason [2], $\varepsilon - \varepsilon_0 = 70000/(T - T_0) =$

$= 7 \cdot 10^3$. If we insert these values into equation (19), $\Delta\varepsilon$ becomes

$$\Delta\varepsilon = -660(\gamma_3 - \gamma_1)\left(1 - \frac{\gamma_3 - \gamma_1}{2}\right)E^2 \tag{20}$$

(where E is given in e. s. u.).

A troublesome situation has existed heretofore for lack of experimental data dealing with the decrease in the dielectric constant of pure $BaTiO_3$ above the Curie point after application of the field. The recent treatment by Siniakov, Stafiichouk and Siniegubova [7] of $BaTiO_3$ ceramic gives the numerical data for a material with an added 0.6 per cent alumina. The Curie temperature of their sample was 125° C. The decrease in the dielectric constant at 10° C. above the Curie point for the weakest of used fields ($E = 3.15$ kV./cm. $= 10.5$ e. s. u.) amount to 600. Thus $\Delta\varepsilon/E^2 = -5.5$. Substituting this value in equation (20) we can find for the anisotropy of the titanium ion-lattice polarizability the reasonable value

$$\gamma_3 - \gamma_1 \cong 10^{-2},$$

i. e. of the same order of magnitude as for the atomic polarizability of some polar molecules (expressed in dimensionless units).

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CHEMISTRY

Anodic Behaviour of Copper in Hydrochloric and Nitric Acid Solutions

by

J. KAMECKI and B. ŁASTOWIECKA

Communicated by B. KAMIEŃSKI at the meeting of June 22, 1953

The anodic behaviour of copper during electrolysis in acid solutions has been the subject of many investigations. Hedges [1], Akimov and Rosenfeld [2] and Bonhoffer [3] took measurements in hydrochloric acid solutions; measurements in nitric acid were made by Hedges [1], in sulphuric acid by Hedges and Müller [4]. It has been noted that copper anodes behave in an interesting way during electrolysis in phosphoric acid. At chosen concentrations and current densities of this acid there follows a polishing of the anodes [5].

The present investigations concern the anodic behaviour of copper in hydrochloric and nitric acid solutions, the methods applied being those described in a previous paper [6]. The measurements consisted in determining the ratio of anodic current density to tension of the electrolysis and in the second series of investigations, the ratio of tension to current density (the electrolysis regulated by tension or by current density). A diagram of the apparatus used is given in Fig. 1.

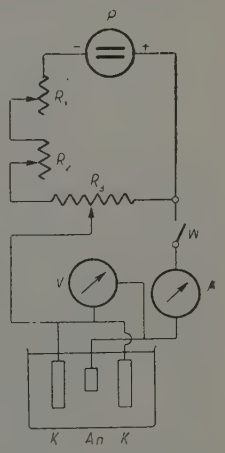

Fig. 1. Diagram of apparatus for measuring the ratio of current density to tension and vice versa

This apparatus was a little different from the earlier one, as rheostats R_1 (with a maximum resistance of 1200 ohms) and R_2 (90 ohms) were joined in series, and R_3 (13 ohms) potentiometrically. Owing to this, it was easier to regulate the tension or current densities. Electrodes of fire-refined rolled copper (99.8% Cu — the same composition as in the previous work) were suspended vertically in acid solution in a glass container with a capacity of c. 420 c. c. in such a manner that the anode was placed between the two cathodes. The surface of the anode was about 31.8 cm.^{2}. The distance between the anode and the cathodes (each $60 \times 40 \times 1$ mm.) was c. 3.5 cm. The glass bath was placed

in a water thermostat maintained at a temperature of $20^0 \pm 0.2^0$ C. The measurements were taken in 5, 3, 1 and 0.01 M solutions of hydrochloric and nitric acid. The tension and the current density were changed at one minute intervals.

The results of the measurements in hydrochloric acid solutions are shown in Figs. 2 and 3, those in nitric acid in Figs. 4 and 5.

The curves representing the ratio of the anodic current density to the electrolytic tension in the 5, 3 and 1 M solutions of HCl show three distinct breaks. The first one, at a tension of about 0.5 V, corresponds to the liberation of hydrogen on the cathodes, the second and the third are induced

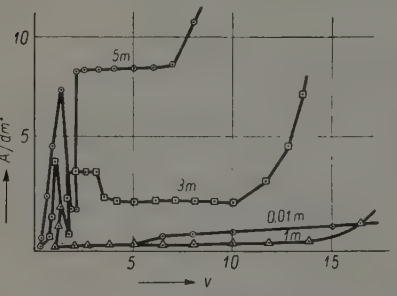

Fig. 2. Curves representing the ratio of anodic current density to tension in 5, 3, 1, and 0.01 M solutions of HCl

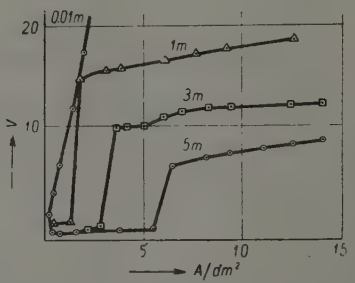

Fig. 3. Curves representing the ratio, of tension to current density in 5, 3, 1 and 0.01 M solutions of HCl

by certain anodic processes. Namely, at a tension of about 1.1 V (in the 5 M solution) and of about 0.8 V (in the 3 and 1 M solutions) a white coating of cuprous chloride begins to form on the anode. With a further gradual increase of tension (to 1.6 V in 5 M and 1.4 V in 3 M solutions) there is a sudden rise in the current density. Then the mean current density remains more or less constant in spite of a further increase of tension to about 7 V, 10 V and 14 V in the 5, 3 and 1 M solutions. During this interval, tension and current density oscillate in regular periods. These oscillations were compensated by continual regulation of the rheostats. At a tension of about 2 V the white coating of the anode began to tarnish, and at a tension of about 6 V and 10 V (5 M and 3 M) to come off in places. At the same time a liberation of gas began on the anode. In the 0.01 M solution a dark coating already began to form at a tension of 0.6 V. After the measurements, the surface of the anode was dull and covered with a dark coating, the more diluted the acid solution, the thicker the covering. This coating could easily be removed.

The curves representing the ratio of tension to anodic current density during electrolysis in HCl solutions show a distinct "jump" in tension (the "jump" was more pronounced the more diluted the acid solution). These "jumps" correspond to the halting points described above. At a density of

0.2—0.6 A/dm.^{2} liberation of hydrogen began on the cathodes, then, at the densities 5.0, 2.8 and 1.3 A/dm.^{2} (in 5, 3 and 1 M respectively) a white coating began to form on the anode (in the 1 M solution this coating darkened rapidly). In the 0.01 M solution the coating was already dark even at a current density as low as 0.3 A/dm.^{2}. Liberation of gas on the anodes was observed at current densities higher than 9, 6 and 5 A/dm.^{2}.

The results described above lead us to the following conclusions: in the case of concentrated solutions, after the critical tension or current

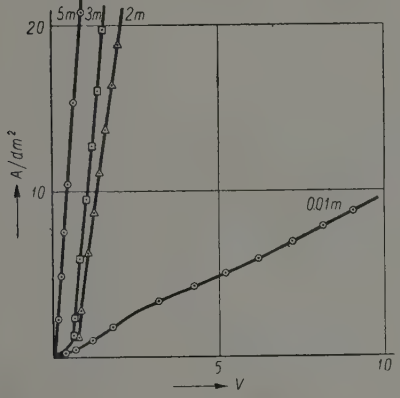

Fig. 4. Anodic current density-tension curves for 5, 3, 1, and 0.01 M solutions of HNO_3

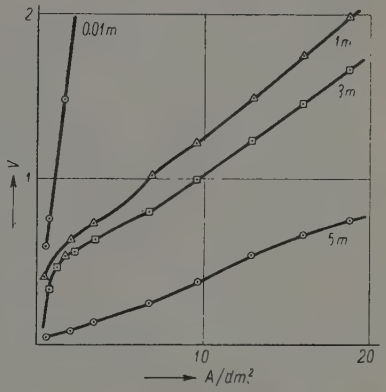

Fig. 5. Tension-anodic current density curves for 5, 3, 1, and 0.01 M solutions of HNO_3

density has been reached, the anode is covered with cuprous chloride. The electric resistance of this cover is low; it is also soluble in hydrochloric acid. At higher current densities (depending on hydrochloric acid concentration) the chlorine ions near the anode drop and copper may become oxidized. The anode covered with the oxide layer becomes passive and there exists a region, as the current-voltage curves show, where the anode resistance is proportional to the tension (voltage); this region is also one of periodic change of tension and current density. When the maximum anode passivity is attained, there occurs a liberation of gas on the anode. In 0.01 M HCl the concentration of chlorine ions is small enough to allow an oxide cover to form almost instantaneously.

Copper anodes dissolved easily in nitric acid at a low tension or current density. The formation of a yellow coating (darker in places) was observed only in the case of an 0.01 M solution at a tension of about 3 V or a current density of about 3 A/dm.^{2}. After electrolysis in 5, 3 and 1 M solutions, the anodes were clean, without any coating, smooth but slightly dull. After electrolysis in 0.01 M HNO_3 the anode was covered with a brownish-yellow coating, closely adhering to the metal. The anode was oxidised, instead of

being dissolved, doubtless owing to the small concentration of nitric ions in 0.01 M HNO_3. The curves given in Figs. 4 and 5 show the influence of polarisation.

Although the anodic density-tension curves in 5 and 3 M HCl were similar to those in phosphoric acid [6], where copper could be polished, the electropolishing in the present solutions was not successful.

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CHEMISTRY

Anodic Behaviour of Copper in Solutions of NaCl, $NaNO_3$ and NaOH

by

J. KAMECKI and B. ŁASTOWIECKA

Communicated by B. KAMIEŃSKI at the meeting of June 22, 1953

In a previous paper [1] a description was given of the anodic behaviour of copper in solutions of hydrochloric and nitric acids, and in a still earlier paper, in phosphoric acid [2]. The present paper is concerned with similar investigations, i. e. with measurements of the relation between the current density on a copper anode and the tension applied to the cathode and anode, and vice versa, in solutions of 3 1 and 0.01 M NaCl and $NaNO_3$ and in solutions of 5, 3, 1 and 0.01 M NaOH. The problem of anodic processes on copper has been dealt with previously, but with the application of other methods by Hedges [3] and Zoltán Szabó [4] in NaCl solutions, and by Hedges [3], Feitknecht and Lenel [5], Hickling [6] and Brouckère [7] in NaOH solutions.

Experimental Section

Apparatus similar to that described in a previous paper [1] was used for measuring. Anodes made of rolled, fire-refined copper were suspended vertically between two cathodes, also of copper. The surface of the anode was c. 32 cm.^{2}, its distance from the cathode about 3.5 cm., the dimensions of each cathode were $60 \times 40 \times 1$ mm. The temperature of the solution during the period in which the measurements were taken was $20^0 \pm 0.2^0$ C.; the anodic tension or density was changed at one-minute intervals. The current was derived from a selenium rectifier.

a. The results of the measurements in solutions of sodium chloride are given in Figs. 1 and 2.

As the tension increased during electrolysis in 3 and 1 M solutions of NaCl, and similarly in the second series of measurements of anodic density, first hydrogen began to be liberated on the cathodes, and then the anode became covered with a yellowish coat, which became darker. A thick yellow colloidal deposit formed on and round the anode. In the 0.01 M solution,

a transient light blue deposit appeared. After electrolysis the anodes were covered with a yellowish deposit in the 3 M solution and with a dark deposit in the 1 and 0.01 M solutions.

In the 3 M solution during the measurements of the ratio of current to tension, regular oscillations appeared in the tension and den-

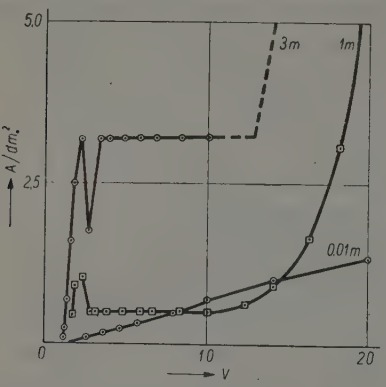

Fig. 1. Curves showing the ratio of anodic current density to tension in 3, 1, and 0.01 M solutions of NaCl

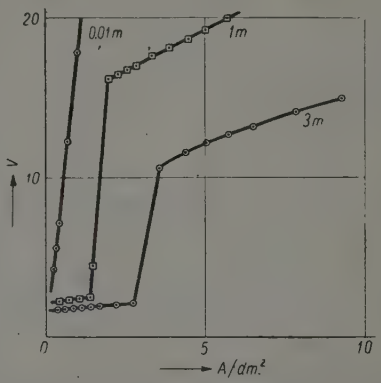

Fig. 2. Curves showing the ratio of tension to anodic density in 3, 1, and 0.01 M solutions of NaCl

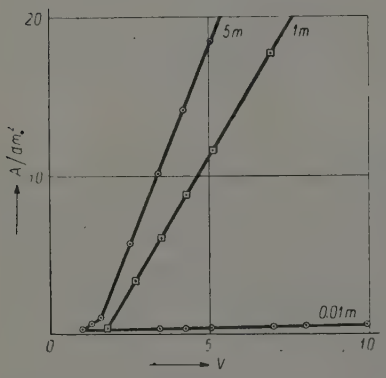

Fig. 3. Curves showing the ratio of anodic density to tension in 3, 1, and 0.1 M solutions of $NaNO_3$

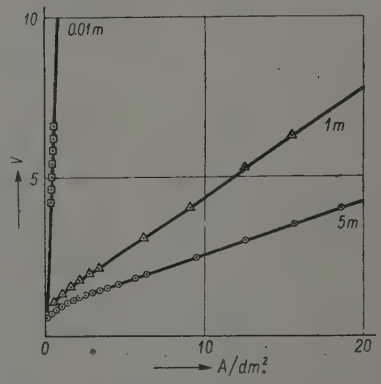

Fig. 4. Curves showing the ratio of tension to anodic density in 3, 1, and 0.01 M solutions of $NaNO_3$

sity. A constant density (horizontal section on the curve-plateau, Fig. 1), was maintained by constantly regulating the resistance of the system. After passing the last break in the curve, oxygen was given off at the anodes.

b In Figs. 3 and 4 the results of measurements in 3, 1 and 0.01 M solutions of $NaNO_3$ are presented in the form of graphs.

In $NaNO_3$ solutions electrolysis proceeded without any perceptibly sudden changes; the anodes dissolved smoothly in the experimental conditions and, after electrolysis, remained clean and smooth, though dulled. During electrolysis the solution took on a blue tint from the copper ions, and a bluish deposit was partially precipitated in the solution; this was specially apparent in the 3 and 1 M solutions.

c. The results of measurements in 5, 3, 1 and 0.01 M NaOH solutions are presented in the form of graphs in Figs. 5 and 6.

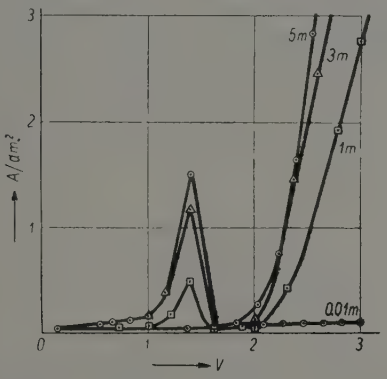

Fig. 5. Curves showing the ratio of anodic density to tension in 5, 3, 1, and 0.01 M solutions of NaOH

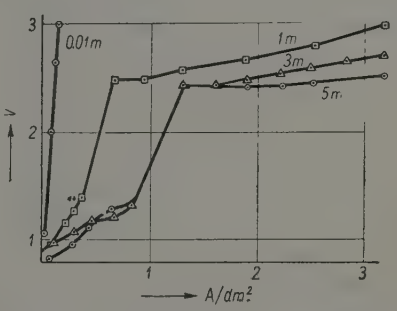

Fig. 6. Curves showing the ratio of tension to anodic density in 5, 3, 1, and 0.01 M solutions

During electrolysis in 5, 3, and 1 M solutions the intensity of current, at first low, began from the moment of hydrogen liberation on the cathodes (c. 1 V) to increase in proportion as the tension was raised. It attained the maximum for a tension of c. 1.4 V, and then once more fell to a low value. It began to rise again from c. 1.8 V with a further increase in tension, when oxygen began to be given off on the anodes. The anodes became covered with a dark coat, which — especially in the 5 and 3 M solutions — was partially dissolved when streaks of a bluish fluid flowed from the anodes and the solution took on a blue tint. After electrolysis in 5, 3, and 1 M solutions the anodes became covered with a greyish-blue coat, which was difficult to remove from the metal. In the 0.01 M solution the anode was coated with a jelly-like, bluish deposit, which could easily be washed off.

Discussion and Conclusions

a. The shape of the curves representing the ratio of anodic density to tension in NaCl solutions and the phenomena arising during electrolysis, may be explained as follows: at low tensions the reaction product is cuprous

chloride, which in practice does not hinder either the flow of the current or the dissolution of the anode. Hydroxyl ions begin to be discharged in proportion as the tension on the anode increases and the anode at first becomes coated at least partially (periodically in the 3 M solution), with a layer of cuprous oxide (or cuprous hydroxide). When a tension of c. 10 V is exceeded, the anode becomes permanently passive and oxygen is given off. The abundant yellow deposit (in 3 and 1 M solutions), forming in the solution round the anode, is probably cuprous hydroxide. In a 0.01 M solution the intensity of the current, as a result of the low ion concentration, and probably as a result of the short period of measurement, is so small that no characteristic phenomena appear. The bluish tint of the deposit which forms in these conditions indicates that the dissolved copper undergoes oxidation, which may be a result of the liberation of OH-ions (possibly also due in part to oxygen from the atmosphere?). Analysis of the shape of the curves representing the ratio of tension to density leads to similar conclusions; the sudden rise in tension caused by the passivity of the anode is seen perfectly in these curves.

b. The course of the curves (Figs. 3 and 4) in 3, 1 and 0.01 M solutions of $NaNO_3$ is similar to that of analogous curves in nitric acid solutions [1]. In 3 and 1 M solutions, a phenomenon probably indicative of cathodic polarization can be observed for low tensions and densities. After a tension of 0.7 – 0.8 V or a density of 0.1 to 0.2 A per dm.^{2} has been exceeded, the further course of the curves — almost a straight line — indicates the smooth course of the electrolysis without passivation of the anode (these conclusions are naturally correct only within the limits of the tensions and densities applied). The products of electrolysis were cupric nitrate (the solutions took on a blue tint) and cupric hydroxide (a blue deposit was precipitated in the solution).

c. The curves in 5, 3 and 1 M solutions of NaOH (Figs. 5 and 6) indicate that initially, as a result of polarisation, only a residual current flows, but, after a tension of 1 V has been exceeded, hydrogen begins to be given off and the intensity of the current increases up to a tension of 1.4 V, whereupon the passivation of the anode begins, probably caused by the appearance of a coat of CuO (darkening of the anode). From the moment when the tension of decomposition of NaOH has been exceeded (c. 1.8 V in the given conditions), there again begins an increase in the intensity proportional to the tension. In the 0.01 M solution, as in the preceding cases, the curves approximate to a straight line and do not enable further conclusions to be drawn, doubtless for the same reasons as have been given above (a.). In no case was polishing of the anodes observed. On the other hand, it was ascertained that in all the cases investigated in this and the preceding research [1], there was, during electrolysis, more marked disso-

lution on the edges and corners of the anodes than on the remaining parts. This is due to the fact that there is greater difficulty in passivating anodes on the corners and edges than on the flat parts.

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CHEMISTRY

The Relation between Half-Wave Potential and Temperature in some Reversible and Irreversible Processes

by

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Communicated by B. KAMIEŃSKI at the meeting of November 16, 1953

Application of the polarographic curves theory is confined solely to reversible processes on a dropping electrode [1]. For this reason, before application of the theory, it is essential in each particular case to establish whether or not the reaction in question is reversible. Two criteria are of prime importance for this purpose: 1) the checking of the relation between $\log(i/(i_d - i)$ and E_K (the potential of the dropping electrode), and 2) the agreement of the half-wave potential $E_{1,2}$ found in the process of cathodic reduction of the given ions with the half-wave potential found in the process of anodic oxidation of the amalgam of the same metal, of which the ions have been previously reduced in the same conditions and temperature. Kolthoff and Lingane [1] have advanced yet a third criterion. They state that in reversible processes the half-wave potential shifts in the direction of a more negative value when there is a rise in temperature; the magnitude of the temperature coefficient should be of the order of 1 mV per degree. In irreversible processes, however, the temperature coefficient should be several times greater and should possess a positive sign. We have found only a few publications [1], [2], [5] which deal with the subject of the experimental verification of these statements, and these are not in agreement as regards the method of measurement. For instance, Nejedly [2] measured the temperature coefficient of the reduction potential, but not the half-wave potential. In view of this, we selected nine different processes in which the half-wave potential and the reversibility (or irreversibility) had previously been measured and confirmed by other workers using different methods.

The measurements consisted in tracing polarographic curves at temperatures of 25°, 35°, 45° and 55° C. and in determining the half-wave potential of the processes in question. The measurements were carried out by means of a polarographic cell, in the shape of a beaker and with a capacity of about 100 ml., as described by Lingane [1], [3]. A bridge, filled with the solution to be tested, connected this cell with an intermediate

one containing a saturated solution of KCl. The latter cell was connected in turn with a saturated calomel electrode. The polarographic cell, the intermediate cell and the saturated calomel electrode were placed in a water thermostat. The air was removed from the polarographic cell by electrolytic hydrogen or by hydrogen from a Kipp's apparatus and put through four wash-flasks, containing respectively 3 per cent $KMnO_4$, 20 per cent alkaline solution of pyrogall, a saturated solution of $HgCl_2$, and water. No differences were observed during the application of either kind of hydrogen. The polarographic curves were registered automatically by a polarograph (Leybolds Nachfolger A. G.), which was complemented by a varying resistance (0—17 ohms) connected in parallel to the bridge of a potentiometric polarograph in order to enable the tracing of the anodic-cathodic waves [4]. The whole arrangement of the apparatus is given in Fig. 1, where *P* denotes the polarograph, *A* the accumulators, *OP* the rheostat (0—17 ohms), *G* the galvanometer, *U* the shunt, *EKR* the dropping mercury electrode, *AN* the mercury anode, *EKN* the saturated calomel electrode, *K* the bridge, *NP* the intermediate cell, and *M* the apparatus for measuring the electromotive force by the method of compensation.

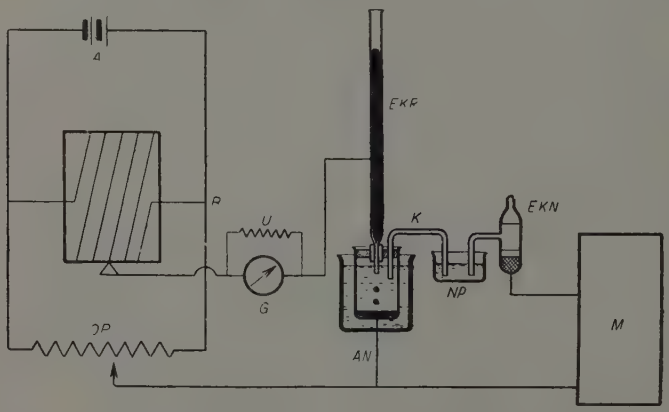

Fig. 1. Arrangement of apparatus for measuring the relation between $E_{1/2}$ and temperature (in relation to a saturated calomel electrode).

For measuring the thermal coefficients the following reactions were chosen:

A. Reversible reactions:

1) $Zn^{++} + 2e \rightarrow Zn$ in 1 M KNO_3;

2) $Fe^{++} \rightleftarrows Fe^{+++} + e$ in 0.5 M potassium oxalate;

3) $Fe^{++} \rightleftarrows Fe^{+++} + e$ in 0.5 M potassium tartrate; the half-wave potentials of reactions 2 and 3 were determined by means of anodic-cathodic waves [1], [4];

4) $Ni^{++} + 2e \rightarrow Ni$ in 1 M $CaCl_2$.

B. Irreversible reactions:

I. $Ni^{++} + 2e \rightarrow Ni$ in 2 M KNO_3 or, to be more exact, the reduction of 6 aquoions $(Ni(H_2O)_6^{++})$;

II. $IO_3^- + 6H^+ + 6e \rightarrow I^- + 3H_2O$ in 0.1 M KOH;

III. $Sn^{++} \rightarrow Sn^{++++} + 2e$ in 0.5 M sodium potassium tartrate + 0.001 M HCl;

IV. $Sn^{++} + 2e \rightarrow Sn$ in 0.5 M sodium-potassium tartrate + 0.001 M HCl;

V. the reduction of ZnO_2^{--} in 1 M NaOH.

In all these solutions the concentration of the reduced or oxidised ion amounted to 10^{-3} gram-ions per litre of solution. For suppression of the maxima, gelatin in a 0.005 per cent concentration was used. A solution of ferrous and stannous salts was introduced into the cell only after removal of the air by means of hydrogen.

The measurements of the potentials of the mercury non-polarizable electrode (large) in relation to a saturated calomel electrode and the voltage corresponding to the half-waves (from polarograms) were carried out several times and the mean values calculated. The values of $E_{1/2}$, i. e. the potentials of the half-wave in relation to a saturated calomel electrode, were calculated from the formula $E_{1/2} = E_A \pm E$, where E_A denotes the potential of the non-polarizable mercury electrode and E the voltage used at the point corresponding to the half-wave. The $-$ sign is used in the case of reduction and the $+$ sign in the case of oxidation.

The results of the measurements of $E_{1/2}$ for particular reactions in relation to temperature are given in Table I.

TABLE I

Potentials of half-wave $E_{1/2}$ in relation to a saturated calomel electrode having the same temperature as the polarographed solution

No. of reaction	Reaction	$E_{1/2}$ in volts at a temperature of			
		25°	35°	45°	55°
	A. Reversible reactions				
1	$Zn^{++} + 2e \rightarrow Zn$	— 1.015	— 1.022	— 1.025	— 1.015
2	$Fe^{++} \rightleftarrows Fe^{+++} + e$ in oxalate	— 0.290	— 0.325	— 0.355	— 0.385
3	$Fe^{++} \rightleftarrows Fe^{+++} + e$ in tartrate	— 0.320	— 0.277	— 0.232	— 0.190
4	$Ni^{++} + 2e \rightarrow Ni$	— 1.065	— 1.055	— 1.047	— 1.035
	B. Irreversible reactions				
I	$Ni^{++} + 2e \rightarrow Ni$	— 1.092	— 1.035	— 1.030	— 1.000
II	$IO_3^- \rightarrow I^-$	— 1.265	— 1.295	— 1.315	— 1.330
III	$Sn^{++} + \rightarrow Sn^{++++}$	— 0.445	— 0.460	— 0.475	— 0.490
IV	$Sn^{++} \rightarrow Sn$	— 0.690	— 0.685	— 0.690	— 0.685
V	$ZnO_2^{--} \rightarrow Zn^{++}$	— 1.512	— 1.515	— 1.520	— 1.475

From the results given in Table I, the temperature coefficients $E_{1/2}$ for each particular range of temperature and the mean values for the range between 25° and 55° were calculated. The results of these calculations are given in Table II.

The potentials of the half-wave measured in relation to a saturated calomel electrode at a temperature of 25° C. are in close agreement with the results obtained by previous workers using solutions of the same composition. For example, for the reactions 1, I and V, we found the values — 1.015, — 1.092 and — 1.512 respectively, while previous workers [1] obtained — 1.012, — 1.1 and — 1.50 V. The values of the temperature coefficients $E_{1/2}$, in those cases where comparison was possible also show a satisfactory agreement: for reactions I and V we obtained the values + 3.0

TABLE II

Temperature coefficients $\Delta E_{1/2}/\Delta T$ in mV per degree

No. of reaction according to Table I	$\Delta E_{1/2}/\Delta T$ in mV per degree within the temperature ranges of			
	25—35°	35—45°	45—55°	25—55° (means)
A. Reversible reactions				
1	−0.7	−0.3	+1.0	0.0
2	−3.5	−3.0	−3.0	−3.2
3	+4.3	+4.5	+4.2	+4.3
4	+1.0	+0.8	+1.0	+0.9
B. Irreversible reactions				
I	+5.5	+0.5	+3.0	+3.0
II	−3.0	−2.0	−1.5	−2.2
III	−1.5	−1.5	−1.5	−1.5
IV	+0.5	−0.5	+0.5	+0.2
V	−0.3	−0.5	+4.5	+1.2

and −3.0 mV per degree, while previous workers give for similar processes +3.3 [1] and −3.0 [5]. On the other hand, neither the sign nor the magnitude of the temperature coefficients for the reactions tested is in agreement with those anticipated by Kolthoff and Lingane [1]. The sign of the temperature coefficient dE/dT in the Gibs-Helmholtz equation can just as well be positive as negative and does not depend upon the reversibility or irreversibility of processes. So the Kolthoff-Lingane criterium of reversibility of electrode processes, based on the temperature coefficient sign and on the magnitude of the half-wave potential cannot be regarded as reliable. This is indicated both by our experimental results and by thermodynamic principles.

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CHEMISTRY

Modification of the Optical Method for Studying Phenomena in the Precritical and Critical Regions of Liquids

by

T. GÜTHNER

Presented by W. ŚWIĘTOSŁAWSKI on January 9, 1954

The optical method for studying phenomena in the critical region has been described in a previous paper [1]. Photographs were taken and a microphotometer was used for determining the width of the shadow stripes in the lower and upper levels of the tube. The modification described in this paper consists in replacing the ordinarily used capillary tubes by ones, whose outside surfaces have been given the forms shown in Fig. 1 (sections a), b) and c)).

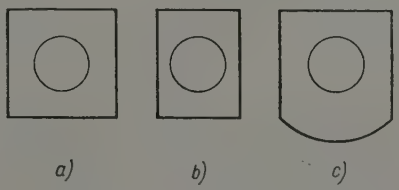

Fig. 1. Sections a), b) and c) of capillary tubes

If the experiments have to be carried out in sealed tubes, then each tube should be placed on a horizontally located milky-white glass plate illuminated by a strong source of light, as previously described [1].

In Fig. 2 is shown an enlarged photographic picture taken at a temperature far removed from the critical one. The large stripe corresponds to the gaseous phase and the narrow one to the liquid phase. The usually observed meniscus is replaced by two "horns" which do not touch each other. A relatively simple relationship exists between the widths of stripes and the refractive indices of both the liquid and gaseous phases for a given length of the wave. Using the Lorentz-Lorenz equation, the densities of the two phases may also be calculated [2].

In Fig. 3 are shown twin apparatus for determining the surface tension of the liquid when a standard liquid is used and when strictly comparative measurements, similar to those described by R. E. Smith and M. Wojciechowski [3] are applied. Each of the twin apparatus should be

Fig. 2. Enlarged photographic picture. Tube filled with ether at 20° C.

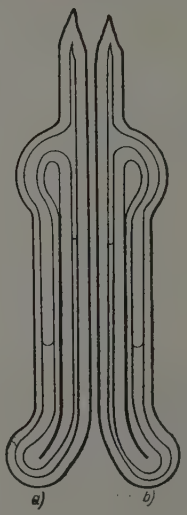

Fig. 3. Twin apparatus for surface tension measurements by comparative method

sealed in order that the surface tension may be determined at any desired temperature even if it be in the close neighbourhood of the critical temperature.

In one set of measurements *a*) is filled with the liquid to be examined in the other *b*) is filled with the standard liquid; in another series of experiments *a*) is filled with the standard liquid and *b*) with the liquid under examination.

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CHEMISTRY

Vitamins and Antivitamins *K*. The Isomeric Monoethers of 3,3′-methylene-bis|6-methyl-2,4-pyronone|

by

I. CHMIELEWSKA and J. CIEŚLAK

Communicated by W. LAMPE at the meeting of December 14, 1953

In the previous paper on the determination of the mechanism of vitamin and antivitamin *K* action, the tautomerism of 6-methyl-2,4-pyronone [1] — analogous to that of benzotetronic acid — has been established. Now, to investigate the tautomerism of the "bis" compounds, 3,3′-methylene-bis|6-methyl-2,4-pyronone| (formula I) [3] was used as a model. According to our hypothesis, the possibility of forming a 4-keto-4-hydroxy group in a system of this type is indispensable for biological activity [4].

The α,γ-pyrone tautomerism of a "bis" molecule would be confirmed by the formation of two monoethers: one with an alcoxyle group in position 2, the other with the same group in position 4. Both compounds have been obtained and their structure determined on the base of the properties described below.

As a result of methylation with diazomethane of 3,3′-methylene-bis |6-methyl-2,4-pyronone| (8 grams) suspended in anhydric ether, two compounds were obtained: the one insoluble (4 grams); the other easily soluble in ether (4 grams).

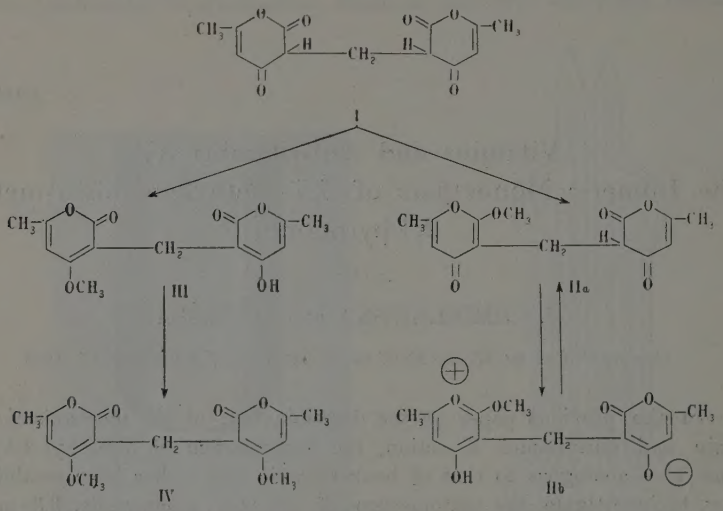
Analyses have proved that the former — m. p. 199—201° C. — was the dimethoxy ether.

Analysis

	calculated for $C_{15}H_{16}O_6$	found
C	61.63%	61.66%
H	5.50%	5.62%
OCH_3	21.20%	20.90%

Both the absorption curve in ultraviolet, typical for α-pyrone systems, and the inability to form a salt with hydrochloride, pointed to the fact that

this compound was 3,3′-methylene-bis[6-methyl-4-methoxy-*α*-pyrone] (formula IV). It therefore corresponds to the already known dimethyl ether of dicumarol [5].



Another methylation product has been separated from the ether solution in the form of crystalline hydrochloride.

Analysis

	calculated for $C_{14}H_{14}O_6$	found
Cl	11.22%	10.90%
OCH_3	9.80%	9.80%

During heating (90—95° C.) this compound has been decomposed into compound I. As shown previously [1], [6], it is a characteristic of the hydrochlorides of 2-methoxy-*γ*-pyrones. After having removed the hydrochloride by means of diethylamine, as described in previous papers [1], [6], a monoether was obtained in the form of a glass-like mass with a low melting point; it has been purified by repeated precipitations with petroleum ether from a solution in anhydrous benzene.

Analysis

	calculated for $C_{14}H_{14}O_6$	found
C	60.43%	60.65%
H	5.07%	4.90%
OCH_3	11.10%	10.70%

The properties of this monoether correspond to those of the already known derivatives of 2-methoxy-*γ*-pyrone [1], [2], [6], [7]: the ability to form hydrochloride (basic character) as well as that to loose the methyl group in-

dicates that the methoxyl group is in position 2 (formula II a). The fact that it is not possible to introduce another methyl group into this monoether by means of diazomethane proves the absence of the free enol group.

Hence, the structure of this ether can be represented either by means of formula II a, or by the tautomeric II b. According to formula II b this

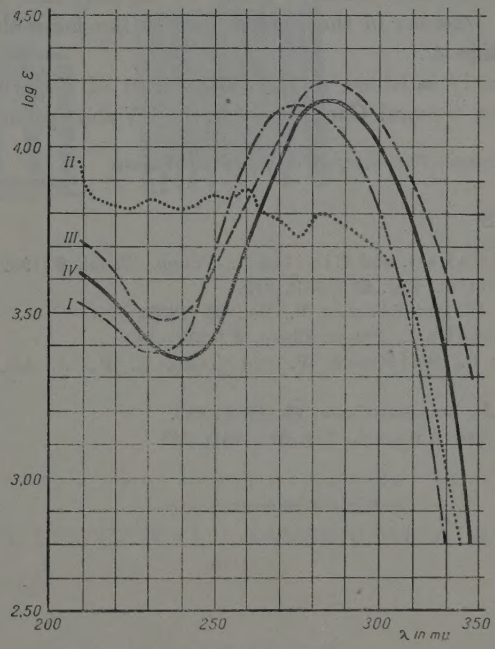


Fig. 1. UV absorption spectra in ethanol.
— • — • — • — compound I,
..... monoether II,
- - - - - - - - - - „ III,
———————— diether IV.

compound would be a polar ion, in which one half of the molecule is a 2-methoxy-γ-pyrone and binds a proton from the second half, which is a 4-hydroxy-α-pyrone. Such a formulation of the structure would explain the absorption curve in ultraviolet, different from the absorption curves of both α and γ-pyrones.

Another monoether, m. p. 147—149° C., has been obtained as a result of methylation of the monosodic salt of the compound with the diazomethane.

Analysis

	calculated for $C_{14}H_{14}O_6$	found
C	60.43%	60.23%
H	5.07%	4.95%
OCH_3	11.10%	10.90%

This monoether does not give a hydrochloride insoluble in ether; on the contrary, it forms salts with bases. Under the influence of diazomethane it is transformed quantitatively into the diether IV — m. p. 199—201° C. — described above. These properties, as well as the UV absorption curve, characteristic for α-pyrone compounds, point to the fact that in this monoether (formula III) the methoxyl group of the first half of the molecule is in position 4, whereas in the second half of the molecule the hydroxyl group is in position 4′.

We are greatly indebted to the Department of Experimental Physics of the Institute of General Chemistry for the UV absorption measurements.

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